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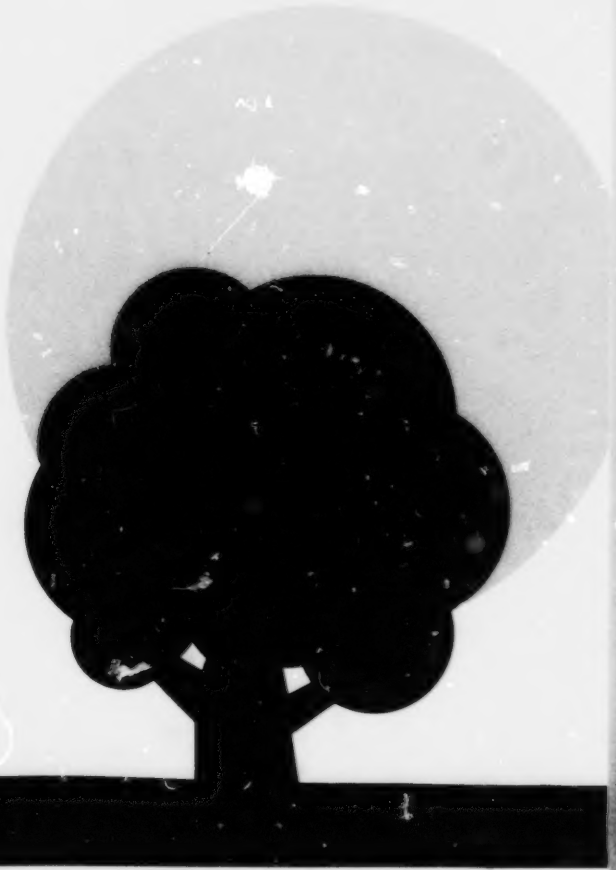

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STUDY OF CONTINUOUS SCREW REACTOR LIQUEFACTION

RENEWABLE ENERGY BRANCH

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1.2 Preface

This report is based on work done on the liquefaction of aspen poplar wood during the period August 1, 1984 to July 1, 1986. Work was also done on the upgrading of the oil produced in the liquefaction process, to produce fuels suitable for use in internal combustion engines and commercially valuable organic chemicals. The conversion of oil produced in the continuous reactor to a product suitable for the upgrading process was investigated, resulting in a suitable process being found. In addition a cost estimate was prepared for the construction of a larger (7.6 cm inside diameter) continuous reactor. Since this project was started in 1979 the report presupposes a background knowledge of material presented in earlier reports. The intention of the report is to give a detailed account of the experimental work done and the results obtained during the study period. The results should serve at least two purposes. Firstly, to provide operating data and the results to be expected for i) the operation of a continuous screw type dry feed reactor to convert aspen poplar to an "oil", ii) the operation of a flow type catalytic reactor to convert, i.e., upgrade, the oil to useful fuels and chemicals, and iii) the treatment (modification) of continuous reactor oil for a suitable feed for the catalytic reactor. Secondly, to provide information which may be used to develop a better understanding of the liquefaction process. Much work remains to be done in all of these areas; liquefaction, upgrading, and an understanding of the liquefaction process. Consequently the results presented here, while hopefully applicable for the conditions used, may be superceded by results obtained using other operating conditions.

The report is intended for use by research workers in this area as well as by those who are interested in the overall picture of the conversion of biomass to useful fuels and chemicals.

1.3 Abstract

Work on the conversion of aspen poplar wood to useful fuels and chemicals has been continued. A continuous reactor using dry feed stock has performed very satisfactorily. Studies on the use of a batch reactor to modify continuous reactor oil to produce a product which may be passed through a fixed catalyst bed has continued. Optimum reaction conditions for this process have been assessed. Treatment of modified continuous reactor oil and batch reactor produced oil to produce benzene and other aromatic hydrocarbons has been studied using various catalysts. A gaseous product is also produced which contains appreciable quantities of both saturated and unsaturated hydrocarbons.

The mechanism of the process whereby the continuous reactor oil is modified in the batch reactor has been studied and some conclusions reached. The importance of the presence of strong reducing agents has been documented.

Some miscellaneous studies included the potential use of spruce wood, aspen wood shavings, corn starch and cellulose as raw materials for the conversion process and an alternate method of carbon analysis of wood oils using a calorimeter. A cost estimate of a similar continuous reactor of 7.6 cm inside diameter has been prepared.

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3.1 Executive Summary

This report describes the results obtained in the period August 1, 1984 to July 1, 1986, of a project investigating the liquefaction of aspen poplar wood to obtain useful fuels and chemicals. This project was one of a number coordinated both nationally and internationally on the liquefaction of biomass. The work consisted of four parts: 1) The treatment, "modification", of continuous reactor oil in the batch reactor, 2) Studies on the mechanism of oil production, 3) Upgrading of modified continuous reactor oil and of batch reactor oil by catalysts using a micro-reactor, 4) The costing of a 7.6 cm (3 in) inside diameter continuous reactor.

The operation of the continuous reactor followed the procedure developed in earlier work. Dry wood meal was fed directly and continuously into a high pressure, ~25 MPa, and high temperature, ~360^{o}C, reactor. Steam and an aqueous solution of sodium carbonate were also pumped into the reactor. Carbon monoxide may also be added. This method appears to be a unique approach to the problem. All other workers in this field either pump liquid slurries of wood and water into a reactor or use some method of vacuum pyrolysis. Batch reactor oil was produced by reacting wood meal, water, carbon monoxide and sodium carbonate in a high pressure rocking autoclave.

Earlier experiments had shoved that oil prepared in the continuous reactor would solidify at 300^{o}C and therefore could not be passed through the catalyst bed of the micro-reactor at 370-390^{o}C which had been constructed to study the parameters involved in the upgrading of the oil into more valuable aromatic hydrocarbons. Therefore, if the continuous reactor oil were to be the source of these aromatic derivatives using the catalytic upgrading it was necessary to modify it so that it could be passed through the micro-reactor. It was found that by heating a mixture of the continuous reactor oil and the accompanying

aqueous phase in the batch reactor, in the presence of carbon monoxide, a product was obtained that contained less oxygen and if passed through the micro reactor over HZSM-5 (zeolite) catalyst gave essentially the same yield of product boiling at or below 218 ^{o}C as when oil prepared directly in the batch reactor was used. Since this two-step approach to converting wood into a potentially valuable raw material for further upgrading to valuable fuel-type chemicals, appeared to be a suitable approach, a study was made of the effect of the various parameters involved in the second modification step. The resulting oil was monitored by an examination of its fluidity, stability to thermal treatment and acetone solubility. The parameters studied were: temperature of reaction, nature and pressure of gaseous phase and time of reaction at the elevated temperature. The optimum conditions were found to be heating the continuous reactor oil with the accompanying aqueous phase at 390 ^{o}C for one hour in the presence of carbon monoxide at an initial pressure of 3.45 MPa.

Although knowledge of these optimum conditions was important for the upgrading process, it was equally important to learn about the chemical mechanism involved in this modification step. Since heating of the continuous reactor oil in water alone did not result in any modification, the aqueous phase contained some component which was involved in the beneficiation. To isolate this component and identify it could have potential value in other upgrading studies. Studies were therefore conducted in an attempt to locate and characterize this component by the techniques of thermal fractionation, ether extraction and ion-exchange chromatography. Although it became clear that the components responsible for the modification were not readily volatile nor ether soluble but water soluble, no further identification was made. By a series of experiments whereby a "synthetic" aqueous phase was first prepared and found to be suitable for use in the modification step, it became clear that

the interaction of water, sodium carbonate and carbon monoxide at 360 ^{o}C generated a reducing solution which was almost, but not quite, as satisfactory as the original aqueous phase. Unfortunately, it was not possible to isolate and characterize the responsible species in this synthetic aqueous phase.

In the upgrading experiments the feed-oil was passed over a catalyst contained in a continuous down-flow fixed bed micro-reactor. Either batch reactor oil or batch reactor modified continuous reactor oil was used as feed. The catalysts used were either HZSM-5, a shape-selective synthetic zeolite material, or various transition metals using either granular carbon or pellitized alumina for a substrate. The weight percent yields of liquid product, of gas produced and of coke formed were determined. The liquid product was vacuum distilled and the yields, based on the original feed-oil, of the distillate and of the remaining residue were measured. The yield of the liquid distillate which boiled in the gasoline range, $\leq$ 218 ^{o}C, was determined. The quantity of aromatic compounds present in this latter fraction was also determined and expressed as a percentage yield based on the original feed-oil. Experiments were done in which water was co-fed with the oil. The effect of water addition was to substantially increase the yield of liquid products and to reduce the amount of coke. A study of the effect of catalyst bed temperature shoved that temperatures in the 370 - 390 ^{o}C range were the most suitable.

Using HZSM-5 as catalyst the highest liquid product yield, in the absence of water feed, was 66.0%. The coke yield was 24.2%. Upon vacuum distillation the yield of liquid in the gasoline boiling point range was 32.4%, based on the original feed-oil, the yield of liquid aromatic compounds was 28.5%. In the presence of water liquid yields of 79.4% resulted, with the coke yield being reduced to 12.4%. Yields of liquid boiling in the gasoline range were as high as 37.4%. Liquid aromatic compounds were obtained in yields as high as 33.0%.

For the transition metal catalysts investigated, the highest liquid product yield, 63.8%, was obtained with ruthenium on alumina pellets. The coke yield was 29.6%. The yield of liquid boiling in the gasoline range was 33.9%, with the yield of liquid aromatic compounds being 17.5%. When water was co-fed the liquid yield was increased to 71.4%, the coke yield was reduced to 23.9%, the yield of liquid boiling in the gasoline range was 35.4% and the yield of liquid aromatic compounds was 19.6%.

A major difference between HZSM-5 and the transition metal catalysts was the substantially larger yields of liquid aromatic compounds produced when HZSM-5 was used.

The gases produced when HZSM-5 was used showed some marked differences from those produced by the other catalysts. Significantly less methane and C_2 hydrocarbons were produced when HZSM-5 was used. However HZSM-5 produced significantly more C_3 hydrocarbons as well as more C_4 hydrocarbons than did the transition metal catalysts.

In planning further work consideration should be given to a study of a prior separation of the oil followed by upgrading of the various fractions. It is quite likely that no single catalyst or set of conditions are suitable for upgrading all of the constituents of the oil.

A 7.6 cm inside diameter continuous reactor, plus auxiliary equipment, contollers and instrumentation was designed and the construction cost estimated. Extrapolating from the current 1.6 cm inside diameter reactor the maximum capacity of the 7.6 cm reactor would be 30.9 kg/hr of wood. At this wood feed rate oil would be produced at a rate of 12.4 kg/hr. The cost of constructing and assembling the 7.6 cm reactor was estimated to be $258 425. A reactor of about this size would seem to be a logical step before a pilot plant was considered. At least two important questions would be answered. Firstly, can wood shavings be satisfactorily converted to oil in reactors of this type? Secondly, will an upscaled feeder work satisfactorily?

3.2 RÉSUMÉ

Ce rapport a trait aux résultats obtenus entre le 1er août 1984 et le 1er juillet 1986 au cours d'un projet qui étudiait la liquéfaction du bois de tremble en vue d'obtenir des combustibles et des produits chimiques utiles. Cette étude s'inscrivait dans le cadre d'un certain nombre de projets coordonnés à l'échelle nationale et internationale sur la liquéfaction de la biomasse. Les travaux comportaient quatre volets : 1) Le Traitement, c.-à-d. la "modification", de l'huile du réacteur à opération continue dans le réacteur à opération discontinue. 2) Des études sur le mécanisme de production d'huile. 3) La valorisation de l'huile modifiée du réacteur à opération continue et de l'huile du réacteur à opération discontinue, au moyen de catalyseurs dans un micro-réacteur. 4) L'évaluation des coûts d'un réacteur à opération continue de 7,6 cm (3 po) de diamètre interne.

Dans le cas du réacteur à opération continue, on a suivi la méthode mise au point antérieurement. La poudre de bois sèche a été introduite directement et de façon continue dans un réacteur à haute pression (~25 MPa) et à haute température (~360°C). On a également pompé dans le réacteur de la vapeur et une solution aqueuse de carbonate de sodium. On peut également ajouter du monoxyde de carbone. Il semble que cette méthode constitue une approche unique au problème. Normalement, on pompe des bouillies de bois et de l'eau dans un réacteur ou bien on utilise une méthode de pyrolyse sous vide. On obtient l'huile du réacteur à opération discontinue en faisant réagir de la poudre de bois, de l'eau, du monoxyde de carbone et du carbonate de sodium dans un autoclave oscillant à haute pression.

Des expériences antérieures avaient démontré que l'huile préparée dans le réacteur à opération continue se solidifierait à 300°C et qu'on ne pourrait donc pas la faire passer sur le lit catalytique du micro-réacteur à 370-390°C. Ce dernier avait été construit pour l'étude

des paramètres liés à la valorisation de l'huile en vue d'obtenir des hydrocarbures aromatiques de plus grande qualité. Par conséquent, pour que l'huile du réacteur à opération continue devienne une source de dérivés aromatiques par valorisation catalytique, il faut la modifier pour qu'elle puisse passer dans le micro-réacteur. On a constaté qu'en chauffant un mélange constitué d'huile du réacteur à opération continue et de la phase aqueuse qui l'accompagne dans le réacteur à opération discontinue, en présence de monoxyde de carbone, on obtien un produit contenant moins d'oxygène. De plus, si on fait passer ce mélange dans un micro-réacteur sur un catalyseur constitué de HZSM-5 (zéolite), on obtient essentiellement le même rendement en produit bouillant à une température inférieure ou égale à 218°C qu'en utilisant l'huile préparée directement dans le réacteur à opération discontinue. Comme cette méthode de préparation en deux étapes semblait appropriée pour transformer le bois en une matière première potentiellement utile pouvant être valorisée par la suite en produits combustibles de grande qualité, on a effectué une étude sur l'effet des divers paramètres intervenant dans la deuxième étape de modification. On a déterminé les caractéristiques de l'huile obtenue, soit sa fluidité, sa stabilité au traitement thermique et sa solubilité dans l'acétone. On a étudié les paramètres suivants : température de réaction, nature et pression de la phase gazeuse et temps de réaction à température élevée. On obtenait les meilleurs résutats en chauffant l'huile du réacteur à opération continue, avec la phase aqueuse qui l'accompagne, à 390°C pendant 1 heure en présence de monoxyde de carbone, à une pression initiale de 3,45 MPa.

Il est important de connaître les conditions optimales du procédé de valorisation, mais il est tout aussi important de connaître le mécanisme chimique intervenant dans cette étape de modification. Du fait qu'on n'observe aucune modification en chauffant l'huile du réacteur à opération continue dans de l'eau pure, la phase aqueuse renferme forcément une substance qui intervient dans la valorisation. La séparation et l'identification de cette substance pourraient être utiles à d'autres études sur la valorisation. On a donc entrepris de localiser

et de caractériser cette substance par fractionnement thermique, extraction à l'éther et chromatographie d'échange d'ions. Même s'il était devenu évident que les substances responsables de la modification n'étaient ni très volatiles ni solubles dans l'éther, mais solubles dans l'eau, les travaux d'identification n'ont pas été poussés plus loin. Au cours d'une série d'expériences pendant lesquelles on a d'abord préparé une phase aqueuse "synthétique", qui s'est avérée appropriée pour l'étape de modification, on a constaté que l'interaction de l'eau, du carbonate de sodium et du monoxyde de carbone à 360°C donnait une solution réductrice qui était presque (mais pas tout à fait) aussi satisfaisante que la phase aqueuse originale. Malheureusement, il n'a pas été possible d'isoler et de caractériser l'espèce en cause.

Au cours des expériences de valorisation, on a fait passer l'huile sur un catalyseur dans un micro-réacteur à lit fixe à courant descendant. On a utilisé l 'huile du réacteur à opération continue ou l'huile modifiée du réacteur à opération continue. Comme catalyseurs, on s'est servi de HZSM-5, une zéolite synthétique morphosélective, ou de divers métaux de transition, en utilisant comme substrat du carbone granulé ou de l'alumine pelletisée. On a déterminé les rendements, exprimés en pourcentage massique de liquide, de gaz et de coke produits. On a distillé le liquide sous vide et déterminé les rendements en distillat et en résidus à partir de la quantité d'huile utilisée au départ. On a déterminé le rendement en distillat liquide bouillant dans l'intervalle d'ébullition de l'essence, à savoir $\leq$ 218°C. On a également déterminé la quantité de composés aromatiques présents dans cette dernière fraction et on l'a exprimée en pourcentage de la quantité d'huile utilisée au départ. Dans certaines expériences, on a utilisé simultanément de l'eau et de l'huile. La présence d'eau augmentait considérablement le rendement en produits liquides et réduisait la quantité de coke. Une étude de l'effet de la température du lit catalytique a démontré que les températures comprises entre 370 et 390°C étaient les plus appropriées.

Lorsque le HZSM-5 était utilisé comme catalyseur, et en l'absence d'eau, le rendement maximal en liquide s'élevait à 66,0 %. Le rendement en coke était alors de 24,2 %. Après distillation sous vide, le rendement en liquide bouillant dans l'intervalle d'ébullition de l'essence était de 32,4 %, par rapport à la quantité d'huile au départ, et le rendement en composés aromatiques liquides était de 28,5 %. En présence d'eau, le rendement en coke tombait à 12,4 %. Les rendements en liquide bouillant dans l'intervalle d'ébullition de l'essence s'élevaient alors à 37,4 %. Pour les composés aromatiques liquides, les rendements s'élevaient à 33,0 %.

Parmi les métaux de transition utilisés comme catalyseurs, c'est le ruthénium sur l'alumine pelletisée qui a donné le rendement le plus élevé en liquide, à savoir 63,8 %. Le rendement en coke était de 29,6 %. Le rendement en liquides bouillant dans l'intervalle d'ébullition de l'essence était de 33,9 % et le rendement en composés aromatiques liquides était de 17,5 %. Lorsqu'on ajoutait de l'eau au départ, le rendement en liquide passait à 71,4 %, le rendement en coke tombait à 23,9 %, le rendement en liquide bouillant dans l'intervalle d'ébullition de l'essence était de 35,4 %, tandis que le rendement en composés aromatiques liquides était de 19,6 %.

La principale différence entre le HZSM-5 et les métaux de transition utilisés comme catalyseurs consistait dans le rendement considérablement plus élevé en composés aromatiques liquides obtenu avec le premier.

Les gaz obtenus avec le HZSM-5 étaient, sous certains rapports, très différents de ceux qui étaient produits avec les autres catalyseurs. En effet, avec le HZSM-5, on obtenait beaucoup moins de méthane et d'hydrocarbures C_2. Cependant, le HZSM-5 donnait beaucoup plus d'hydrocarbures C_3 et C_4 que les métaux de transition.

Dans la planification des travaux futurs, il faudrait prévoir une étude comportant une séparation préalable de l'huile, puis la valorisation des diverses fractions. Il est peu probable qu'un seul catalyseur ou qu'un seul ensemble de conditions conviennent pour la valorisation de tous les constituant de l'huile.

On a conçu un réacteur à opération continue, de 7,6 cm de diamètre interne, ainsi que le matériel accessoire, les systèmes de régulation et les instruments, et on a évalué le coût de construction. Si l'on extrapole les résultats obtenus avec le réacteur actuel, dont le diamètre interne est de 1,6 cm, on obtient une capacité maximale de 30,9 kg bois/h pour le réacteur de 7,6 cm, ce qui corespond à une production d'huile de 12,4 kg/h. On a évalué à 258 425 $ le coût de la construction et de l'assemblage du réacteur de 7,6 cm. Il semble logique de construire un réacteur de ces dimensions avant d'envisager la construction d'une usine pilote. Cela permettrait au moins de répondre a deux questions importantes. Premièrement, est-il possible de transformer de façon satisfaisante des copeaux de bois en huile dans les réacteurs de ce type? En second lieu, un dispositif d'alimentation de plus grandes dimensions donnera-t-il des résultats satisfaisants?

4.1 INTRODUCTION

In a period when fossil hydrocarbons are likely to become scarcer and much more costly (inspite of the current "glut" of petroleum, which is at least partially artificial), methods to convert renevable biomass to useful fuels and chemicals feedstocks are becoming increasingly attractive. All such biomass is composed of two chemically different components; the carbohydrate based holocellulose (cellulose and hemicellulose) and the aromatic based lignin, which together have a much lower heating value than fossil fuels due to their high oxygen content. The production of a fuel competitive with natural oil must therefore involve significant oxygen removal.

A process to accomplish this oxygen removal is that based on the early research of Appell et al. (7) at the U.S. Bureau of Mines. These workers reported that a variety of lignocellulosic materials (wood products, agricultural and civic wastes) could be converted, in part, to a fuel oil by reaction with carbon monoxide and water at elevated temperatures in the presence of sodium carbonate. It was of interest to determine if a typical hardwood such as aspen poplar of which Canada has large, virtually unused, resources could be treated similarly to produce a useable oil. Work to produce an "oil" from Saskatchevan aspen poplar wood has been described in an earlier report (1). Several unanswered questions arose out of this earlier work and the work described in this report was undertaken to find answers to some of these questions.

4.2 OBJECTIVES

The following are the main objectives of the current project:

1) To study the use of various catalysts in a micro-reactor to upgrade the oil to useful fuels and chemicals.
2) To develop a method of treating, "modifying", continuous reactor oil in the batch reactor to obtain a product which could be passed through the micro-reactor.
3) To study the mechanism of oil production.
4) To estimate the cost of constructing a 7.6 cm inside diameter continuous reactor.

4.3 PROCEDURE AND RESULTS

4.3.1 Using the continuous reactor

The continuous reactor, which has been described in an earlier report (1), was used principally to produce an oil fraction for subsequent modification (described below), in the batch reactor, to obtain the feed for upgrading studies (described below). Some preliminary work was done in an attempt to process spruce wood meal and a mixture of spruce and aspen wood meals.

4.3.1.1 Preparation of oil from aspen poplar wood

A total of twelve runs was made in order to prepare sufficient oil for subsequent modification in the batch reactor. For eleven runs the reactor was pressurized with carbon monoxide and for one (C-57)[1] nitrogen was used instead of carbon monoxide. In each run the system was pressurized initially to 20.7 MPa and during a run the pressure was controlled at 22.8 - 24.1 MPa. A five percent sodium carbonate solution and steam were pumped into the reactor at rates shown in Table 1. The reactor temperature was maintained at 360 ^{o}C. A typical analysis of the product oil showed ~68.0% carbon and ~6.5% hydrogen and, by difference, ~25.5% oxygen.

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[1] In this report the letter C is used to designate continuous reactor runs, replacing SC used in earlier reports.

One other run (C-63) was made using the standard conditions except that the 5% sodium carbonate solution was replaced by the combined aqueous solutions from run B-414 and B-415 (see Section 4.3.3.5.2)(Table 3).

4.3.1.2 Processing of spruce wood meal

Attempts were made to process spruce wood meal in the continuous reactor, using the same operating conditions as for the aspen wood meal. One run used only spruce wood and two runs used a mixture of equal parts of spruce wood and aspen wood. In all cases the runs were unsuccessful because the motor stalled, approximately five minutes into the run, due to a high torque being developed in the screw. Clearly a modification to the existing screw design would be required in order for spruce wood to be processed successfully. This study was abandoned.

4.3.2 Using the batch reactor

The batch reactor, which has been described in an earlier report (2), was used to produce oil samples for upgrading studies, to study the effect of process variables on the wood-to-oil conversion process, to initiate studies on the reaction mechanism of the modification process and for other miscellaneous purposes described below.

4.3.2.1 Direct wood conversion in the batch reactor

Several samples of oil (runs B-364, B-367 to B-369 (referred to as B-367 oil), B-379 and B-380 (referred to as B-379 oil), B-383, B-387 to B-390 (referred to as B-387 oil), B-391 to B-394 (referred to as B-391 oil)) were made for use in subsequent up-grading studies in the catalytic micro-reactor that was described earlier (1,3). The conditions used for all runs were: aspen wood meal (100 g), sodium carbonate (2%, 500 mL), initial carbon monoxide pressure (3.45 MPa) heated to 390^{o}C for one hour. The product oils were essentially the same with an average yield of 34.4%, and analyzing (average)

for C, 80.8%, H, 7.7%. The oil, on heating to 400°C remained fluid, became solid on cooling and the cooled product was moderately soluble in acetone. One further run (B-382) was made under similar conditions except that a temperature of 360°C was used. A very fluid oil (31.5 g) was produced containing 4.3% moisture and analyzing for C, 80.3; H, 7.4%. A sample of this oil, on heating to 400°C remained fluid and on cooling was moderately soluble in acetone.

4.3.2.2 Modification of continuous reactor oil

4.3.2.2.1 Determination of optimum conditions

Work described in the earlier report (1) had indicated that continuous reactor oil was unsuitable for upgrading via catalytic micro-reactor processing. This oil solidified upon preheating to reactor temperature (380 °C) and, therefore, could not be passed through the micro-reactor. If, however, oil from the continuous reactor were re-processed by heating it in the batch reactor in the standard sodium carbonate solution, in an atmosphere of carbon monoxide, it then was stable to 400 °C and could be upgraded satisfactorily. Consequently, a number of runs were made to determine the optimum conditions for this "re-processing" or "modification" step. The mass of continuous reactor oil used in each run was approximately 50 g. The mass of product obtained was approximately equal to the amount of continuous oil used. A summary of these runs is given in Table 2.

4.3.2.3 Preparation of oil from IEA wood

In response to a request from B.C. Research (Dr. J. Howard) for a sample of oil made from the standard aspen wood that had been supplied by IEA (International Energy Agency), five batch runs were made. A total of 173 g of fluid oil (4.0% moisture) was obtained and which analyzed for C, 80.3%, H, 7.0% and, by difference 0, 12.7%. The conditions used for each run were: IEA wood (6-8% moisture) (100 g), sodium carbonate (2%, 500 mL), initial pressure of

carbon monoxide (3.45 MPa), heated to 360 °C for one hour. The average yield was 34.6% on a dry weight basis.

4.3.2.4 Attempted preparation of oil using CO_2 instead of CO

Since it was known that carbon dioxide is formed during the liquefaction process, one run (B-324) was made except that carbon dioxide was used instead of carbon monoxide. The conditions used were: aspen wood meal (100 g), sodium carbonate (2%, 500 mL), initial carbon dioxide pressure (3.45 MPa) heated to 360 °C for one hour. The run was not successful: only 3.1 g of a very viscous and tarry dry oil (C, 74.2%; H, 8.1%) was produced from 100 g wood.

4.3.2.5 Attempted preparation of oil from corn starch and cellulose

One run (B-363) was made under the following conditions: corn starch (technical grade) (100 g), sodium carbonate (2%, 500 mL), initial pressure of carbon monoxide (3.45 MPa), heated to 360 °C for one hour. The resulting dry oil (C, 69.9%; H, 7.1%; O (by difference), 23%) was obtained in 34.0% yield but was mostly a gummy tar with only a small amount of fluid oil present. The gas produced in the liquefaction process contained 38% CO_2, 40% Co and 22% H_2.

One run (B-365) was made under the same conditions as B-363 but cellulose (100 g) replaced the corn starch. The resulting dry oil (C, 72.8%; H, 7.3%; O (by difference) 19.9%) was obtained in 30.7% yield and was very fluid. The gas produced in the liquefaction process contained 58% CO_2, 3% CO and 42% H_2.

4.3.2.6 Preparation of oil from aspen wood shavings

One run (B-384) was made using aspen wood shavings (100 g) under the same conditions as B-363 except that the temperature was 390 °C. The resulting dry oil (C, 84.8%l; H, 7.9%; O (by difference), 7.3%) was very fluid.

4.3.3 Studies on the mechanism of modification of continuous oil

From results on the studies on the batch modification of continuous reactor oil (see Section 4.3.2.2) it was apparent that the original aqueous phase produced concurrently with the oil in the continuous reactor contained

some component which was responsible for the subsequent successful modification in the batch reactor. Studies were initiated in an attempt to isolate, and later identify, this fraction. Run B-396 (see Table 3), in which continuous reactor oil was successfully modified using the aqueous phase from the same run as produced the continuous oil sample, served as a reference standard for the modification experiments.

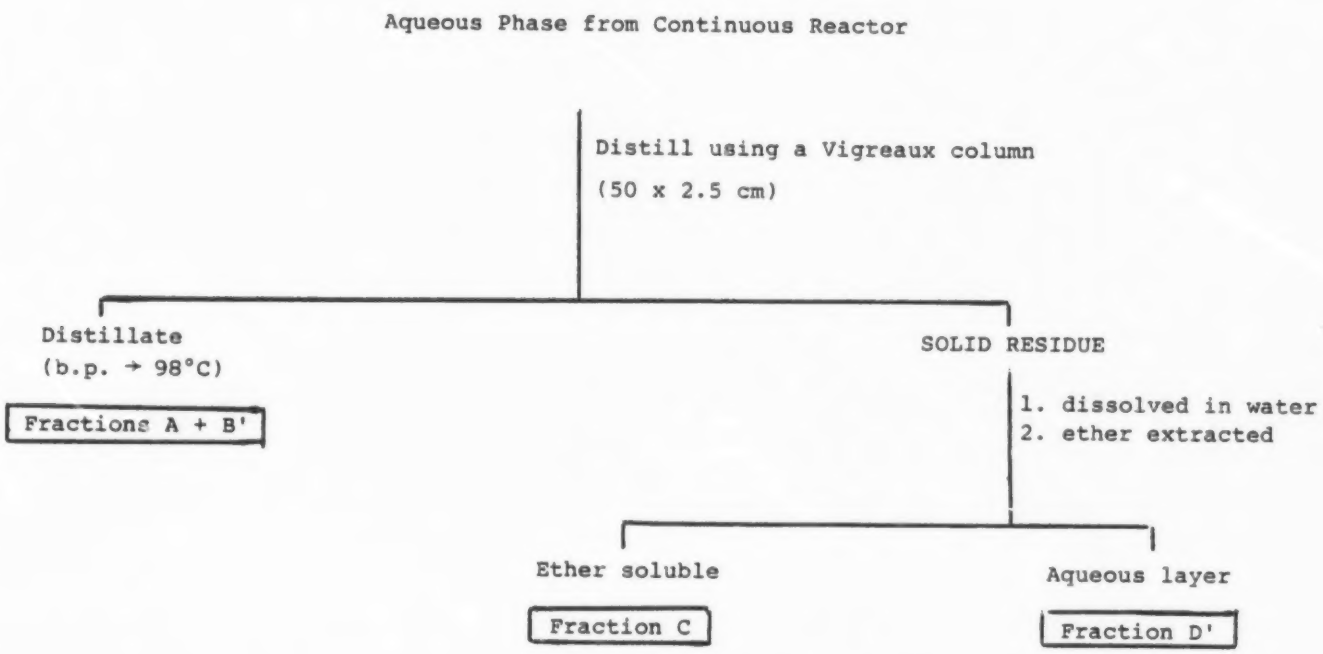
4.3.3.1 Fractionation of the aqueous phase

In an attempt to gain some insight as to which constituents of the aqueous phase are responsible for the modification process; aqueous phases from the continuous-reactor run C-55 (Table 1), batch reactor runs B-357 and B-359 (Table 2) were fractionated according to the separation procedure reported previously (4). The results are given below.

Fraction	Wt of fraction in 500 g of aqueous phase		
	Run C-55	Run B-357	Run B-359
A	1.1	3.9	2.6
B	12.9	8.9	8.0
C	23.4	4.3	8.5
D	23.8	13.4	14.6
E	11.3	0.3	0.8
TOTAL	72.5 g	30.8 g	34.5 g

The aqueous phase in both runs B-357 (C-55 oil) and B-359 (no oil) was from the continuous reactor run C-55. Comparing these data, the most profound changes resulting from the reprocessing of the original aqueous phase, are the reduction in the relative amounts of Fractions C, D and E. Although this observation has not been explained apparently more components of Fraction C react when oil is present than when it is absent.

One run B-356 was subsequently made using the oil from run C-58, a mixture of the fractions A, B, C and D obtained from the aqueous phase of Run C-55, at an initial pressure of CO of 3.45 MPa, for one hour at 390 ^{o}C. The resulting oil was very fluid, and analyzed for C, 80.3%; H, 7.4%. The temperature of polymerization was 380 ^{o}C and gave a product which was only slightly soluble in acetone. All subsequent fractionations were made using a similar, but simplified, procedure. This procedure is outlined below.



[NOTE: Fractions have been relabelled to distinguish them from designations used in the original publication (4)].

Using the separate fractions indicated above, runs (B-395 --> B-398, B-400) were made in an attempt to modify the continuous reactor oil in the batch reactor. The mass of continuous reactor oil used in each run was approximately 50 g. The mass of product obtained was approximately equal to the amount of continuous oil used. The conditions used for each run are given in Table 3.

4.3.3.2 Role of formic acid in modification process

In earlier studies (4), appreciable amounts of formic acid had been identified in the aqueous phase. To test the potential role of formic acid in the modification process, Runs B-399, B-401 and B-404 were made and are described in Table 3.

4.3.3.3 Attempted isolation of active modifying component by ether extraction

Experiments were made to determine if any component(s) in the aqueous phase that was(were) responsible for the beneficial modification was(were) ether-soluble. Three separate 500 mL aliquots of an aqueous phase were extracted with ether using a continuous liquid - liquid extractor for four days, with fresh ether being used for the fourth day. After drying, the ether was removed and the residues kept at 0 ^{o}C. The details are given in Table 4.

Table 4. Weight (g) of Ether Residues

Run No.	1	2	3
3 days	35.2	28.2	18.0
4th day	1.84	3.27	4.55
Total	37.04	31.47	22.55

NOTE: In run 3, the aqueous phase was not initially shaken in the storage container before the 500 mL sample was withdrawn.

Two batch modification runs were made using in one case (B-402) the ether extract from Run 1 dissolved in water (500 mL) (pH = 2) and in the other case (B-403) the residual aqueous layer of Run 1 after ether extraction and after standing overnight to allow the ether to evaporate.

4.3.3.4 Attempted isolation of active modifying component by ion exchange procedure

It was of interest to determine if the components of the aqueous phase which were responsible for the successful modification (see Section 4.3.2.2.1) could be separated and isolated by passage of the aqueous phase through a protonated ion exchange column packed with REXYN 101 packing. The residual aqueous phase, after ether extraction, of run 2 (Table 4) (425 mL, pH 4) was passed slowly through the column and followed by a water wash until the eluate was pH 5-6. This total combined solution, of volume 1600 mL, was concentrated to a volume of 500 mL (pH 2) and a distillate (pH 3). A batch modification run (B-405, Table 3) was made using this 500 mL concentrate and another run (B-406, Table 3) was made using 600 mL of the distillate.

The results obtained from these two runs were inconclusive. It was felt that the excessive amount of water that had been used for washing the resin after the aqueous phase was passed through had a negative effect on its subsequent use. An attempt was made using methyl orange indicator to determine the resin void volume but it was unsuccessful. An estimate was then made assuming that the resin bed consisted of close-packed spheres. The value of the void volume was ~135 mL.

In earlier work some qualitative tests were made using $Ba(NO_3)_2$ and $Ag\ NO_3$ to determine if any soluble material (acids?) could be precipitated. Negligible precipitate was formed using the $Ba(NO_2)_3$ but a silver mirror was produced using $Ag\ NO_3$ shoving the presence of reducing agents. This test was

then used to monitor the eluate from the ion exchange resin column. The formation of the silver mirror would indicate that the eluate still contained material from the original aqueous phase.

Water was allowed to pass through the protonated column until its level reached the top of the resin. The aqueous phase (500 mL) from run 3 (Table 4) was poured onto the column, aliquots collected and tested for reducing power by adding one mL of $AgNO_3$ solution to one mL of eluate. The results are given in Table 5.

Table 5. Results of ion exchange separation

Aliquot No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Time (min)	9	15	10	35	108	25	15	20	25	25	32	40	35	33
Volume (mL)	50	50	25	125	200	125	50	50	25	25	50	50	50	50
pH	6	6	3	2	2	2	2	2	2	3	3	3	3	4
Amount of mirror formed[a]	N	N	S	L	L	L	L	L	L	L	S	S	S	S

[a] Legend: N (none); S (small); L (large)

A combination of aliquots 4 to 10 inclusive (600 mL) was then used as the aqueous phase for an oil modification run (B-406, Table 3). A second similar run was also made (B-408, Table 3).

4.3.3.5 The role of reducing agents in oil preparation

4.3.3.5.1 Batch modification of continuous reactor oil

Following the recognition (see Section 4.3.3.4) that a strong reducing agent, as revealed by the silver mirror test, was present in the aqueous phase from runs made using the continuous reactor, it was of interest to determine if these agents came only from the reagents used (Na_2CO_3, CO, water) or were associated with the wood meal.

A series of runs (B-407, B-409, B-410, B-412, B-413, Table 3) was made whereby the reducing aqueous solution was first prepared and then used in attempts to modify the continuous reactor oil. Runs B-414 and B-415 were made to prepare the reducing aqueous solution for use in the continuous reactor (see Section 4.3.3.5.2).

4.3.3.5.2 Direct wood liquefaction

One run (B-411, Table 3) was made in which the previously prepared reducing solution (B-410) was used to liquefy wood in the batch reactor. Another run (C-63, Table 1) was made using the combined aqueous solutions from runs B-414 and B-415, Table 3) in an attempt to liquefy wood in the continuous reactor).

4.3.4 Oil upgrading

This section describes experiments designed to catalytically convert the wood-derived oil to liquid fuels and other valuable organic compounds. The apparatus and procedure have been discussed in a previous report (1) and will not be repeated here. Two types of feed oils were used: the batch-modified continuous reactor oils (4.3.2.2) and oils prepared in the batch reactor (4.3.2.1).

In many of the upgrading experiments the shape-selective catalyst HZSM-5 was used. This was prepared in our laboratories according to the procedure described in the patent literature (5) and was the same as that used in the upgrading work previously reported (1).

In runs U47[1] to U82 using the small micro-reactor (diameter 0.635 cm) (1), each experiment consisted of two duplicate runs, eg., U47 and U48. This was

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1. In this report the letter U is used to designate upgrading runs, replacing PR used in earlier reports.

necessary to collect sufficient upgraded product for analysis. For each duplicate pair of runs the oil products were mixed together and vacuum distilled at 66.7 Pa (0.50 torr) and 200 °C.

4.3.4.1 Batch-modified continuous reactor oils

Five experiments were made, all at a temperature of 370 °C and using a VHSV (volume hourly space velocity) value of 2. The catalyst used was HZSM-5. The same batch oil, B-367, was used in all of the experiments. The conditions used and the results obtained are given in Table 6.

4.3.4.2 Batch reactor oils

4.3.4.2.1 Effect of temperature

Six experiments were made to investigate the effect of temperature on the products obtained in the upgrading process. The VHSV value was 2 in all of the experiments except in the pair of runs U71/72 where the value was 4. Temperatures used were 350 °C, 370 °C and 390 °C. The catalyst used was HZSM-5. The conditions used and the results obtained are given in Table 7.

4.3.4.2.2 Effect of addition of water

Previous work (1) had indicated that the addition of water to the feed to the micro-reactor resulted in the production of significantly less coke, more gaseous unsaturates and a larger yield of residue remaining after vacuum distillation of the liquid product.

Four experiments were made in which the water:oil ratio was varied from 0 to 3:1. Temperatures of 370 °C and VHSV values of 4 were used. The catalyst used was HZSM-5. The conditions used and the results obtained are given in Table 8.

4.3.4.2.3 Use of various catalysts[1]

In this series of experiments the following catalysts were used: HZSM-5, 0.5% palladium on 4-8 mesh granular carbon, 0.5% palladium on 0.318 cm (1/8 in) alumina pellets, 0.5% platinum on 0.318 cm alumina pellets, 0.5% rhodium on 0.318 cm alumina pellets, and 0.5% ruthenium on 0.318 cm alumina pellets. In addition 3 mm glass beads were used as an "inert" packing for the catalytic reactor. A temperature of 370°C was used in the work.

The original micro-reactor, 0.635 cm diameter, was used in one pair of duplicate runs, U81 and U82, with 0.5% palladium on 4-8 mesh granular carbon as the catalyst. In this pair of runs a VHSV value of 4 was used. All of the other experiments used a 1.27 cm diameter reactor and a VHSV value of 2.5. In these experiments only a single run was required to furnish sufficient upgraded product for analysis. Water was added to the feed in two of the experiments, U91 and U92. The conditions used and the results obtained are given in Tables 9 and 10.

To assist in deciding whether or not the glass beads used in run U90 did behave as an "inert" material a sample of the feed oil, B-391, was vacuum distilled and the quantities of products obtained were compared with those obtained in run U90. The results are given in Table 11.

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1. The catalysts, other than HZSM-5, were supplied by Engelhard.

Table 11

Comparison of vacuum distillation of B-391 oil and of treating B-391 oil in the micro-reactor using glass beads.

	Vacuum distillation of B-391 oil	U90[a]
% liq. product vac. dist.	54.1	57.0
% residue of vac. dist.	45.9	41.8[b]
% total liq. product boiling $\leq$ 218°C	30.9	34.9
% total liq. product boiling $\leq$ 218°C and aromatic	15.6	19.6

[a] See Table 10.

[b] Sum of % "coke" (17.9) and % residue of vac. dist. (23.9), see Table 10.

4.3.5 Alternate method of analysis of carbon in oil samples

Oil samples are a complex mixture and some of the components are volatile at room temperature. If an attempt is made to analyze a fresh oil sample in the C-H analyser the continued loss of volatile components does not enable the sample weight to be accurately determined. Consequently the samples were allowed to stand exposed to the atmosphere for at least a week before being analyzed. Such treatment allows an accurate sample weight to be found, however volatile components have been lost which may have a different carbon content than the average value for the original oil. The sample boat used in the

analyser results in a large exposed surface area to sample volume, aiding in loss by evaporation. It is not possible to enclose the oil sample while it is being weighed. An oil sample was sent to a commercial laboratory, using an automatic analyzer, but they refused to continue the analysis after the first sample "flashed" and contaminated the analyser. Consequently, an alternative method of carbon analysis was investigated using the Parr Calorimeter.

In this procedure, 0.8 g of a sample, either the liquefaction oil or an authentic reference compound, was burnt in the presence of excess oxygen (2.5 MPa) in the calorimeter. The resulting carbon dioxide was passed into a known, excess quantity of standardized sodium hydroxide. Subsequently, the carbonate was precipitated as barium carbonate by the addition of barium chloride solution, and the excess alkali titrated with standard hydrochloric acid. These data permitted of the calculation of the carbon content of the sample (Table 12). To test the reproducibility of this analytical procedure, ten replicate analyses were made using the oil (2.65% moisture) prepared in the batch reactor and referred to as B-387 oil (see Section 4.3.2.1). The percentages of carbon obtained were 80.5, 81.0, 81.5, 80.6, 80.0, 80.3, 79.5, 79.0, 80.7 and 80.5%; giving a mean value of 80.4% with a standard deviation of 0.7.

4.4 DISCUSSION OF RESULTS

4.4.1 Using the continuous reactor

The small-scale laboratory continuous reactor has continued to run very successfully. During the period of this contract a total of thirteen runs have been conducted, ranging in running time from two to six hours. In total, 17,557 g of aspen poplar wood meal were processed over a period of 51.75 hours to yield over six kilograms of an oil (see Table 1). The reproducibility of the procedure in the apparatus was well proven. Unfortunately, attempts to use

spruce wood meal were unsuccessful since a high torque developed resulting in motor stoppage. No explanation of this difference between the two species of wood can be given. A modification of the existing screw design to accommodate the difference in the fibre structure may be the solution.

4.4.2 Using the Batch Reactor

4.4.2.1 Direct Wood Conversion

A total of sixteen runs were made using aspen wood meal in the batch reactor (see Section 4.3.2.1). The oil so produced was used in further upgrading studies using the catalytic micro-reactor (Section 4.3.4).

A further five runs (see Section 4.3.2.3) used the standard aspen wood that had been supplied by the IEA (International Energy Agency). There was no perceivable difference in the oil so produced and that obtained, under similar conditions, using local aspen poplar. A sample was forwarded to Dr. John Howard, B.C. Research, for analysis under the Canadian Biomass Development Program (BDP). No results have been reported.

Three other exploratory runs were made (see Section 4.3.2.5 and Section 4.3.2.6). It was of interest to compare the suitability of both the readily available, abundant and chemically similar raw materials, cellulose and corn starch, as oil precursors. Although the yields and analysis of the products were similar, there was a marked difference in their physical forms. The product from cellulose was a very fluid oil but that from starch was mostly a gummy tar. The significant difference, too, in the composition of the residual gas cannot be explained. Both observations suggest that, in the case of cellulose, the conversion reaction, using CO, is predominant and this may be related to both the stereochemistry of the linkages involved and the chemical nature of the monosaccharide units making up the polymeric raw material.

The exploratory run (see Section 4.3.2.6) using wood shavings instead of wood meal was very successful. This observation was very important since it is most likely that shavings would be the form of raw material used in any scaled-up industrial plant (see Section 5.1.1).

4.4.2.2 Modification of Continuous Reactor Oil

Work described in the earlier report (1) had indicated that continuous reactor oil was unsuitable for upgrading (production of aromatic hydrocarbons) via catalytic (HZSM-5 zeolite) processing. The oil solidified upon preheating to reactor temperature (380°C) and, therefore, could not be passed through the micro-reactor. If however the oil were first reprocessed by heating it in the batch reactor with the standard sodium carbonate solution in an atmosphere of carbon monoxide, it was converted into a product which was then stable to 400°C. Furthermore it had been shown that if the oil and the accompanying aqueous phase from a continuous reactor run were reheated in the batch reactor at 360°C for one hour an improved oil was produced and could be processed in the micro-reactor. An extensive series of runs (Table 2) was made in an attempt to determine the optimum conditions for this reprocessing. Each run was monitored by an examination of the appearance of the resulting oil; a small sample was heated in air to determine if it could be heated to 400° without polymerization (a necessary property if it were to be upgraded in the micro-reactor) and its solubility in acetone (reflecting the degree of polymerization). As a result of these studies the following conclusions were drawn:

a) Reprocessing at 390°C instead of 360°C gave a better product with a higher carbon content (run B-325).

b) The ratio of aqueous phase to oil is important (runs B-326, B-329, B-344).

c) Carbon dioxide is unsatisfactory (run B-327).

d) Good agitation of the reactor is important (run B-330).

e) Adequate carbon monoxide is necessary (runs B-331, B-341, B-342).

f) Replacing the aqueous phase by water only (run B-332, B-340), water containing sodium formate (run B-333), or water buffered to pH4 (run B-345) were unsatisfactory. It appeared that pH alone was not the critical parameter, even though the pH of the original aqueous phase was around 5.

g) The effect of variation of treatment time was investigated (runs B-334 (0h), B-353 (0.5h), B-349 (1.0h) and B-351 (4.0h)). A minimum of one hour was required to produce satisfactory oil, but further heating for a total of four hours did not result in any significant difference.

h) The presence of carbon monoxide is necessary as shown by runs B-335 to B-337, B-339 in which combinations of nitrogen and carbon monoxide were used or run B-358 and in which hydrogen was used.

i) Bubbling air through the aqueous phase (run B-343) or through both aqueous phase and oil (run B-348) had little effect on the modification process.

As a result of these studies it was apparent that the optimum conditions for modifying the continuous-reactor oil were those reported earlier (1), in which the aqueous phase of a continuous-reactor run along with the oil fraction were reprocessed at 390°C in the presence of carbon monoxide (3.45 MPa initial).

4.4.2.3 Mechanism of modification of continuous reactor oil

From the results on the studies on the batch modification of continuous reactor oil (see Section 4.4.2.2) it was apparent that the original aqueous phase produced concurrently with the oil contained some component(s) which was (were) responsible for the successful modification in the batch reactor. Studies were initiated to attempt to isolate this fraction.

Using first the procedure for separation of the components in the aqueous phase that had been reported earlier (4) (see Section 4.3.3.1), it was shown (run B-386, Section 4.3.3.1), that by a recombination of all the separated components in an aqueous phase the modification was successful. Subsequently, using the simplified procedure (see Section 4.3.3.1), it was shown that if Fractions A, B′, C and D′ were recombined and used as the aqueous medium (run B-400) a successful modification could be made. However, if only Fraction A and B′ (run B-395), or Fraction C (run B-397) were used, modification was poor. It appeared, then, that Fraction D′ contained the reactive modifying component, but run B-398, using Fraction D′, was only partly successful.

Realizing that the aqueous phases from the continuous-reactor oil were acidic (pH 4-5), and knowing (4) that formic acid was a product of the wood conversion process, some runs (B-399, B-401, and B-404) were made using solutions of formic acid. The modification was moderately successful and appeared to confirm the acidic requirement. Attempts to isolate the active component(s) by ether extraction of the aqueous layer, and subsequent use in modification runs (run B-402), were unsuccessful. However the non-ether soluble residue continued to function well in the modification procedure (run B-403).

Having determined that the reactive components were highly water soluble, and likely of an acidic nature, attempts were made to separate them by the passage of the aqueous phase, after ether extraction, through a protonated cation exchange column and subsequently using the eluate in a modification run (runs B-405, B-406). The results were inconsistent and only moderately successful.

In some preliminary attempts to isolate, from the aqueous phase of a continuous-reactor run, the components which contributed to the subsequent successful modification in the batch reactor, it was found that the addition of $AgNO_3$ resulted in the production of a silver mirror. This was strong evidence

for the presence, in the aqueous phase, of reducing agents and which may well be the active components that were being sought. Subsequently, this test was used to monitor the presence of these active components, as, for example, during the ion exchange separation discussed above. By reacting together only water, sodium carbonate and carbon monoxide at both 360 ^{o}C (runs B-410, B-412, B-414 and B-415) or at 390 ^{o}C (run B-407) it was readily shown that the reducing agents were produced from these reactants and not as a result of the interaction with the wood. It was thus of interest to determine if continuous-reactor oil could be modified in the batch reactor by using the preformed reducing solutions instead of the aqueous phase resulting from the continuous-reactor run. The product so produced (runs B-409 and B-413) had properties similar to those of the oil produced using an aqueous phase (run B-385) but was less thermally stable.

An attempt to use the preformed reducing solution (runs B-414 and B-415) in a run (run C-63, Table 2) to convert aspen wood in the continuous-reactor was unfortunately not successful in producing a thermally stable oil. It had been thought that the increased concentration of the reducing agents at the moment of contact with the wood meal might have resulted in a oil similar to that produced by modification in the batch reactor.

Although these studies have provided some further insight into the mechanisms of the beneficiation of the continuous-reactor oil by a subsequent reaction in the batch reactor, no specific component(s) that are responsible has (have) been isolated.

4.4.3 Oil Upgrading

4.4.3.1 HZSM-5 Catalysts

HZSM-5 is a porous, acidic, shape-selective catalyst with a regular pore structure. Consequently it has the ability to convert mixtures of high

molecular hydrocarbons, and oxygenated hydrocarbons, into lower molecular weight aromatics, alkenes and alkanes. This typical behavior is seen in the results of the upgrading experiments reported in Tables 6, 7 and 8.

4.4.3.1.1 Upgrading of batch modified continuous reactor oil

In order to treat continuous reactor oil in the micro-reactor it was necessary to modify it in the batch reactor as described in section 4.3.2.2.1. Upgrading studies were done using batch modified oils B-349, -351 and -358. The conditions used for the preparation of those oils are given in Table 2. The conditions used and the results obtained in the upgrading experiments are given in Table 6.

Runs U51/52 are repeats of runs U47/48 as are runs U53/54 of runs U49/50. These runs were repeated because problems with the analyses of the earlier runs caused the results to be questioned. There appears however to be satisfactory agreement between the two pairs of duplicate runs. The results give some idea of the reproducibility of the upgrading experiments.

The results show that the use of the catalyst HZSM-5 can result in the feed oil being converted to a liquid product boiling at or below 218^{o}C in a 24-32% yield. The yield of aromatic compounds in this boiling point range being 22-29%, based on the original feed oil. The gases produced are particularly rich in C_3 and C_4 hydrocarbons, which has commercial implications.

It is of interest to note that while runs U49/50 and U53/54 gave a higher yield of vacuum distilled liquid product, and a smaller amount of residue after vacuum distillation, than did runs U47/48 and U51/52 they gave lower yields of total liquid product and of aromatic product boiling at or below 218^{o}C. The feed oil, B-351, used in runs U49/50 and U53/54 had been modified by heating for 4 hours whereas the feed oil, B-349, used in runs U47/48 and U51/52 had been modified by heating for the usual 1 hour period. Apparently heating for 4

hours in the modification step resulted in a larger fraction of higher molecular weight compounds which while they vacuum distill at 66.7 Pa and 200°C do not boil at or below 218°C at atmospheric pressure.

Duplicate runs U57 and U58 used as feed oil B-358 which had been modified using a 3:2 mixture of CO and H_2. The results do not appear to be significantly different from runs using feed oils which have been prepared using CO in the modification step.

4.4.3.1.2 Upgrading of batch reaction oils

Since it was less time consuming to use oils prepared directly from wood meal in the batch reactor for the upgrading studies the use of such oils for this purpose was started. The preparation of these feed oils is given in section 4.3.2.1.

4.4.3.1.2.1 Effect of temperature

The results of varying the micro-reactor temperature are given in Table 7. A temperature of 350°C is not nearly as satisfactory as either 370°C or 390°C. At 350°C the yield of liquid product is significantly smaller whereas the yield of coke is significantly larger. The use of 390°C appears to be marginally better than 370°C. The yield of liquid product, of liquid product boiling at or below 218°C and the yield of aromatic products boiling at or below 218°C are all somewhat higher at 390°C than at 370°C whereas the yield of coke is less.

The decrease in the weight percentage of coke produced as the temperature increases is rather surprising, since coking usually increases with increasing reactor temperature. However, in this case, other reactions may be accelerated by a temperature increase faster than the coking reaction. An increase in temperature also leads to the production of relatively more lower-boiling products, as both the gas production and the liquid products boiling at or below 218°C are larger at higher temperatures. Also within the gas product

itself there is a minor shift to lover molecular veight compounds. From these results the use of higher temperatures could seem to be desirable because of the lover coke production and the higher percent conversion to gasoline-range compounds.

Runs R67/68 and U69/70 are replicates of runs U63/64, the agreement is good, especially between the first two sets of runs.

Runs U71/72 indicates that there is little effect of increasing the VHSV from 2 to 4 on the upgrading results. The use of a larger VHSV value does however result in the duration of a run being shorter for the through put of the same amount of feed material.

4.4.3.1.2.2 Effect of the addition of water

In a previous report (1) it was noted that the addition of water to the feed to the micro-reactor resulted in pronounced differences in the products obtained. One of the most sigificant differences being a pronounced decrease in the amount of coke produced together with an increase in the amount of liquid product. Studies using canola oil have also shown similar effects (6).

Table 8 gives the results obtained in the present work when water was co-fed with batch reactor oils through a micro-reactor using HZSM-5 as the catalyst.

There was an average decrease of 62% in the amount of coke produced when the water to oil ratio was varied from zero to 3:1. The amount of gas produced increased only slightly as water is added, indicating that it cannot only be the gasification of the coke by steam which is responsible for the amount of coke produced. The use of water resulted in an average increased yield of liquid product of 21%. Upon vacuum distilling the liquid product the yield of liquid distillate was increased by an average of 8.2% and the residue by 12.9%.

The yield of identified aromatic compounds, boiling at or below 218°C increased by an average of 18.3%. There are also significant shifts to higher molecular weight compounds in the gas product coupled with the production of relatively more unsaturated compounds. All of the above effects are desirable. The largest change observed was that in going from zero water to a water to oil ratio of 0.55:1. Furthermore the largest yield of aromatics boiling at or below 218°C was produced when the water to oil ratio was 0.55:1. Apparently some water, but not too much, is optimum.

Runs U86 (Table 9) and U91 (Table 10), made using the larger, 0.635 cm diameter, micro-reactor show similar results when the water to oil ratio is varied from zero to 1:1.

4.4.3.2 The use of various catalysts.

Tables 9 and 10 give the results of using various catalysts, including HZSM-5. Two experiments, U91 and U92, were also done where water was co-fed with the oil.

An attempt was also made to find out the effect at 370°C of passing the oil through a catalyst free micro-reactor. To accomplish this 3 mm glass beads were used as packing. While not completely unambiguous it would appear that the result was similar to that of a vacuum distillation of the feed oil. The "coke" produced was quite different than that with the catalysts, in that it softens upon heating and is soluble in acetone. The coke produced on the catalysts does not soften upon heating and is insoluble in acetone. Table 11 compares the results of vacuum distillation of the feed oil and of passing the feed oil over the glass beads (run U90). In this table the value given for the % residue of vacuum distillation of the product of run U90 is the sum of the values for the "coke" produced and the residue of vacuum distillation given in Table 10. The two sets of results in Table 11 agree quite well. Also

consistent with the idea that run U90 produced results similar to vacuum distillation is the fact that no detectable amounts of CO or of CO_2 were produced. In addition the volume of gas produced in this run is small compared to the volumes produced when catalysts were used.

For all of the catalysts used, including HZSM-5, the weight percentages of liquid, gas and coke produced did not show great variations. A possible exception is ruthenium on alumina pellets, run U88, which gave the largest yield of liquid, 63.8%, and the lowest coke yield, 29.6%.

The gases produced by HZSM-5 did however show some marked differences from those produced by the other catalysts. HZSM-5 produced significantly less methane and C_2 hydrocarbons than did the other catalysts. However HZSM-5 produced significantly more C_3 hydrocarbons as well as more C_4 hydrocarbons than did the other catalysts.

When water was co-fed using ruthenium on alumina pellets, run U92, the result was an increase in the yield of liquid product and a decrease in the yield of coke.

The results given here are probably more important for the questions raised than for the facts found. It seems evident that a more thorough study should lead to improved yields of desirable products. It is quite possible that prior separation of the feed oil, perhaps by vacuum distillation, would yield fractions each of which would be found to react differently to a given catalyst. It is perhaps worth repeating from a previous report (1) that it was found the air condensed fraction from the vacuum distillation of batch reactor oil is relatively inactive with HZSM-5. Hence in a more detailed study various fractions of the oil should be treated with different catalysts.

4.4.4 Alternate method of analysis of carbon in oil samples

The oil samples produced from wood are a complex mixture and some of the components are volatile at room temperature. If an attempt is made to analyze a fresh oil sample in the C-H analyzer the continued loss of any volatile components does not enable the sample weight to be accurately determined. An alternative method was investigated (see Section 4.3.5) whereby the sample was burnt in a Parr Calorimeter in the presence of excess oxygen and the resulting carbon dioxide determined by volumetric analysis. The method had an acceptable degree of reproducibility and gave results which compared satisfactorily to the calculated values of pure compounds or to those for the oil samples if determined by standard C-H analysis.

5.1 COST ESTIMATION OF A 7.6 cm CONTINUOUS REACTOR

Mr. G. Dyck, who had designed and supervised the construction of both the semi-continuous and the continuous reactor, was asked to design and estimate the cost of construction and assembly of a 7.6 cm (3 inch) inside diameter continuous reactor. The assumptions which he used are given in Section 5.1.1.

5.1.1 Assumptions

1. The wood will be fed as shavings in which the moisture content has been reduced to 10% by air drying.
2. An auger speed of 30 rpm.
3. Capacity of the 7.6 cm reactor. With the current 1.59 cm I.D. reactor the wood feed rate is 22.4 g/min at an auger speed of 30 rpm. Assuming that the rate of through-put is proportional to the cross-sectional area then the scale up factor is $(7.6 \text{ cm}/1.59 \text{ cm})^2 = 23$. Hence the capacity of the 6.7 cm reactor would be 22.4 g/min x 23 = 515 g/min. This value corresponds to 30.9 kg/hr of wood.
4. A 40% conversion of wood to oil. At a wood feed rate of 30.9 kg/hr the rate of oil production would be 12.4 kg/hr.

5. Na_2CO_3 requirement. Using a Na_2CO_3: wood ratio of 0.04:1 the weight of Na_2CO_3 could be 1.24 kg/hr.

6. CO requirement. We do not know the amount of CO actually used up in the process. The initial charge in the current reactor is 8.19 mole. This value corresponds to 5.22 kg of CO for the 7.6 cm reactor.

7. Steam requirement. Using a water:wood ratio of 2:1 and allowing for the water contained in the wood (10%) and in the Na_2CO_3 solution the steam feed rate comes to 51.5 kg/hr.

8. The heat load is to be applied by the steam. Using heat capacities of wood, Na_2CO_3, CO and the average heat content of water at the working conditions the total heat load is calculated to be 168, 970 kJ/hr (160, 260 BTU/hr.). This value includes an estimate of the heat losses. If this heat requirement is to be supplied by steam at 27.6 MPa (4000 psi) then the heat content of the steam is estimated to be 3277 kJ/kg (1410 BTU/lb).

5.1.2 Cost estimates (1986 dollars)

1) Reactor-feeder unit

a) 3-stage auger (feeder)	$15,000
b) reactor augers	6,000
c) stainless steel compression sleeve	2,000
d) cast iron compression sleeve	1,200
e) steel casing for compression sleeve assembly	5,000
f) stainless steel reactor tube	10,000
g) feeder mechanism	3,000
h) hydraulic auger removal tool	2,000
TOTAL	$44,200

2)	Collector vessels	
	Two collector vessels, each approx. 5L capacity	$20,000
3)	Motor drive assembly	
	2000 ft-lb x 5 hp	$ 2,600
4)	Base, on which unit sets	$ 2,000
5)	Gas storage unit, approx. 50L capacity	$10,000
6)	Protective walls for reactor room	$ 3,000
The following costs were obtained from various equipment suppliers.		
7)	Conveyor belt	
	For lifting wood shavings to top of feeder unit	$ 2,200
8)	Compressor, for CO	$13,000
9)	Pumps	
	a) Na_2CO_3 solution	$ 6,400
	b) H_2O for steam generator	$25,000
10)	Demineralizer, for water	$ 1,300
11)	Furnace and controls. For steam production.	$39,860
12)	Wood planar	$ 1,900
13)	Piping, valves, fittings	$12,680
14)	Controllers/instrumentation	$20,000
15)	Insulation	$ 300
16)	Wood storage containers	$ 400
17)	Water storage containers	$ 500
18)	Mixer for preparing Na_2CO_3 solution, storage	$ 900
19)	Oil storage/separators	$ 500
	Total equpment costs	$206,740
	Installation cost (est. 20% of equipment costs)	41,348
	Contingency (est. 5% of equipment costs)	10,337
	Total capital cost	$258,425

6.1 TABLES

Table 1. Preparation of Oil Using the Continuous Reactor

Run	Time	Wood Used		Sodium Carbonate (5%)	Ratio	Steam	Ratio
	h	Total	Rate	Rate	Na_2CO_3:Wood	Rate	Water:wood
		g	g/mm	mL/min		g/min	
C-48	2.25	797[a]	5.9	4	0.033:1	8	2.0:1
C-50	3	981	5.9	4	0.033:1	8	2.0:1
C-52	2.5	802	5.3	4	0.036:1	8	2.2:1
C-53	4	1275	5.3	4	0.036:1	8	2.2:1
C-54	6	1984	5.5	4.4	0.038:1	7.3	2.1:1
C-55	6	1984	5.5	4.2	0.037:1	7.5	2.1:1
C-57[b]	3	1064	5.9	4.7	0.038:1	7.3	2.0:1
C-58	6	2117	5.9	4.7	0.038:1	7.2	2.0:1
C-59	2	703	5.9	4.4	0.036:1	7.3	1.9:1
C-60	3	1026[a]	5.7	4.4	0.037:1	7.2	2.0:1
C-61	6	2052	5.9	4.4	0.036:1	7.3	2.0:1
C-62	6	2019	5.9	4.4	0.036:1	7.3	2.0:1
C-63	2	753	5.9	4.4[c]	0.036:1	7.3	2.0:1

a. Calculated from rate and time.

b. Nitrogen gas used instead of carbon monoxide.

c. The 5% sodium carbonate solution was replaced by the combined aqueous solutions from Runs B-414 and B-415 (see Section 4.3.3.5)

Table 2. Determination of optimum conditions for Batch-Modified Continuous Oil[a,b,c,d]

Run	Reaction Conditions		Description of Product					Remarks
			Aqueous Phase		Oil Phase			
	Oil Source	Liquid Phase	pH	Appearance	Appearance	Effect of Heating in Air		
						Temp. of Polymerization	Solubility in Acetone[e]	
B-325	C-44	C-44 aq. phase	5		uniform, very fluid	400	s	C, 84.8%; H, 7.9%
B-326	C-48	C-48 aq. phase (250 mL)	5		~70% very fluid, rest very viscous	unsuitable		C, 82.1%; H, 7.5%
B-327	C-48	C-48 aq. phase	5		not uniform, tarry, viscous	unsuitable		CO_2 used at 360 °C
B-329	C-48	C-48 aq. phase (250 mL)	5		mostly fluid, some chunks	unsuitable		C, 82.6%; H, 8.1%
B-330	C-48	C-48 aq. phase	5		not uniform, mostly chunky, some fluid	unsuitable		C, 67.5%, H, 6.5% Reactor was not shaken
B-331	C-50	C-50 aq. phase	5		not uniform, very viscous tar	unsuitable		CO pressure 0.69 MPa C, 77.7%; H, 7.6%
B-332	C-50	water	5		not uniform, very viscous, partly fluid	unsuitable		C, 82.1%; H, 8.3%
B-333	C-50	water containing sodium formate (6.4 g)	7		very viscous, tarry and fluid	unsuitable		C, 76.0%; H, 7.2%
B-334	C-50	C-50 aq. phase	5		fairly uniform, slightly viscous	390 °C	ss	Time (0 h) C, 78.4%; H, 7.0%
B-335	C-50	C-50 aq. phase	5		viscous, tarry, charry	charred at 280 °C	ss	N_2 used C, 71.9%; H, 6.5%
B-336	C-50	C-50 aq. phase	5		partly fluid, partly viscous and tarry	unsuitable[f]		CO (0.69 MPa) and N_2 (2.76 MPa)
B-337	C-52	C-52 aq. phase	5		mostly very fluid, some viscous	400 °C	s	CO (2.07 MPa) and N_2 (1.38 MPa)
B-338	C-52	C-52 aq. phase	5		uniform and very fluid	400 °C	vs	

Table 2. Continued .....

Run	Reaction Conditions		Description of Product					Remarks
	Oil Source	Liquid Phase	Aqueous Phase		Oil Phase			
			pH	Appearance	Appearance	Effect of Heating in Air		
						Temp. of Polymerization	Solubility in Acetone[a]	
B-339	C-52	C-52 aq. phase	5		partly very fluid, partly viscous, some char	charred at 290 °C	ms	N_2 used
B-340	C-52	water	5		moderately viscous, some char	unsuitable		
B-341	C-53	C-53 aq. phase	5		very fluid, some tar and char	unsuitable		CO (2.07 MPa) used
B-342	C-53	C-53 aq. phase	5		uniform and very fluid	400 °C	vs	CO (2.76 MPa) used
B-343	C-53	C-53 aq. phase	5	dark brown	uniform and very fluid	400 °C	vs	air passed into aq. phase for 1 h prior to use
B-344	C-53	C-53 aq. phase	5		uniform, very fluid, little tar	400 °C	s	Aq. phase (400 mL)
B-345	C-53	Acetic acid - sodium acetate buffer (pH 4)	4.5		tar, small amount oil	unsuitable		
B-348	C-54	C-54 aq. phase	5	clear, colourless	uniform, fluid	385 °C	ss	C, 78.8%; H, 7.5% Air passed into oil and aq. phase for 1 h prior to use
B-349	C-54	C-54 aq. phase	5	clear, blue tinge	uniform, very fluid	400	s	C, 78.3%; H, 7.3%
B-350	C-54	Aq. phase from B-349 (490 mL)	5.5	clear, dark blue	chunky, tarry, very little oil	unsuitable		C, 81.3%; H, 7/2%
B-351	C-54	C-54 aq. phase	5.5	clear, pale blue	uniform, very fluid	400	s	Time (4 h) C, 80.3%; H, 7.6%
B-353	C-54	C-54 aq. phase	5	clear, pale blue	uniform, fluid	400 °C	ss	Time (0.5 h) C, 80.7%; H, 7.5%
B-354	C-54	C-54 aq. phase (400 mL)	5.5	opaque, black	uniform, very fluid	400 °	vs	Time (0 h); CO (2.76 MPa) Temperature (410 °)

Table 2. Continued ...

Run	Reaction Conditions		Description of Product					Remarks
	Oil Source	Liquid Phase	Aqueous Phase		Oil Phase			
			pH	Appearance	Appearance	Effect of Heating in Air		
						Temp. of Polymerization	Solubility in Acetone[e]	
B-355	C-54	C-54 aq. phase	5	clear, pale green tinge	uniform, fluid, little char	400 °	ms	Air passed into oil and aq. phase for 4 days prior to use
B-356	C-54	C-54 aq. phase (400 mL)	5	clear, green-grey	uniform, fluid	400 °	s	CO (4.14 MPa) used
B-357	C-55	C-55 aq. phase	5	clear, green tinge	uniform, fluid	400 °	vs	
B-358	C-55	C-55 aq. phase		clear, colourless	uniform, fluid	400 °	vs	CO (2.07 MPa) H_2 (1.38 MPa) used
B-359	None	C-55 aq. phase	5	clear, pale yellow	very little, very fluid	unsuitable		
B-360	C-55	C-55 aq. phase	5	clear, pale yellow	little fluid oil bulk very viscous and tarry	unsuitable		H_2 (3.45 MPa) used
B-376	C-57	C-57 aq. phase	5	clear, slightly greenish	very fluid with some small chunks	400 °	ms	
B-377	C-57	C-57 aq. phase	5	clear, slightly greenish	very fluid, grainy	400 °	ms	
B-378	C-58	C-58 aq. phase	5	Clear, slightly greenish	very fluid	400 °	ms	C, 82.3%; H, 7.5%
B-381	C-58	C-58 aq. phase	5	clear, slightly greenish	very fluid	400 °	ms	C, 80.7%; H, 7.1%

[a] Gas phase was CO unless otherwise noted. Initial gas pressure was 3.45 MPa.

[b] Temperature of reaction was 390 °C unless otherwise noted.

[c] Liquid phase was 500 mL unless otherwise noted.

[d] Time of heating at 390 °C was one hour unless otherwise noted.

[e] Solubilities expressed as: ss - slightly soluble (< 10%)
ms - moderately soluble (~ 35%)
s - soluble (~ 60%)
vs - very soluble (> 90%)

[f] Unsuitable due to a lack of uniformity as a result of being a mixture of oil and solid particals.

Table 3. Batch modifications re study of active modifying component

Run	Reaction Conditions		Description of Product					Remarks
	Oil Source	Liquid Phase	Aqueous Phase		Oil Phase			
			pH	Appearance	Appearance	Effect of Heating in Air		
						Temp. of Polymerization	Solubility in Acetone	
B-385	C-59	C-59 aq. phase	5	clear, greenish tinge	very fluid oil, few small chunks	400	ms	
B-395	C-60	C-60 fractions A+B' (460 mL, pH 2) plus water 40 mL	4	clear, colourless	viscous tar, little fluid	400	ms	
B-396	C-60	C-60 aq. phase	5	clear, black	very fluid	400	ms	
B-397	C-60	C-60 fraction C made to 500 mL	5	clear, greenish tinge	viscous tar	375	ss	
B-398	C-60	C-60 fraction D' made to 500 mL	7	clear, turned black	partly viscous, partly fluid	400	ms	
B-399	C-60	formic acid (5 g) in water (500 mL) adjusted to pH 5 with NaOH	6	clear, dark grey	moderately fluid	390	ss	
B-400	C-60	C-60 recombined fractions A,B',C and D', made to 500 mL	5	clear, turned black	very fluid oil	400	ms	
B-401	C-61	formic acid (10 g) in water (500 mL) adjusted to pH 3.5 with NaOH	6	clear, black	uniform, fluid	400	ss	
B-402	C-61	ether extract (37 g) of aq. phase of C-61 made to 500 mL (pH 2)	4	clear, greenish tinge	chunky fluid and viscous, little char	390	ss	
B-403	C-61	aq. phase of C-61 after ether extraction	7		very fluid	385	ss	

Table 3. Continued ....

Run	Reaction Conditions		Description of Product					Remarks
	Oil Source	Liquid Phase	Aqueous Phase		Oil Phase			
			pH	Appearance	Appearance	Effect of Heating in Air		
						Temp. of Polymerization	Solubility in Acetone	
B-404	C-61	formic acid (5 g) and C-61 aq. phase (250 mL) made to 500 mL (pH 3)	5	dark with greenish tinge	uniform, moderately fluid	395	ss	
B-405	C-61	C-61 aq. phase after ether extraction, passage through ion exchange, concentrated to 500 mL	6	clear, turned black	uniform, but viscous (gas bubbles)	385	ms	
B-406	C-61	distillate from concentration of B-405 (600 mL)	4	clear, greenish tinge	very viscous	390	ss	
B-407	None	Na_2CO_3 (10 g) in water (500 mL)	7	clear				
B-408	C-61	C-61 aq. phase after ether extraction, passage through ion exchange	4	clear, greenish tinge	moderately fluid	390	ss	
B-409	C-61	aq. phase from Run B-407 (pH 8)	6	black	uniform, very fluid	385	ss	
B-410	None	Na_2CO_3 (10 g) in water (500 mL)	7	clear				360 °C
B-411	Wood	aq. phase from B-410 (pH 7)	7	black	fluid, smooth	380	ss	360 °C

Table 3. Continued ...

Run	Reaction Conditions		Description of Product					Remarks
	Oil Source	Liquid Phase	Aqueous Phase		Oil Phase			
			pH	Appearance	Appearance	Effect of Heating in Air		
						Temp. of Polymerization	Solubility in Acetone	
B-412	None	Na_2CO_3 (10 g) in water (500 mL) (pH 12)	7	clear				360 °C
B-413	C-61	aq. phase from B-412	7	black	fluid, smooth	370	ss	
B-414 B-415	none	Na_2CO_3 (25 g), water (500 mL) (pH 12)	8	clear with fine brown suspension after 1 day				

Table 6. Upgrading experiments: upgrading of batch-modified continuous reactor oil[a,b]

Run Number[c]	U47/48	U49/50	U51/52	U53/54	U57/58
Variables:					
Feed Oil	B-349[d]	B-351[e]	B-349[d]	B-351[e]	B-358[f]
Temp (°C)	370	370	370	370	370
Duration (h)	1	1	1	1	1
VHSV	2	2	2	2	2
wht % liq produced	66.0	62.6	56.1	59.7	54.0
wht % gas produced[g]	9.8	7.7	6.3	4.4	5.4
wht % coke produced	24.2	29.7	37.6	35.9	40.6
Analysis:					
relative to feed oil					
% liq product vac dist	48.4	54.3	42.9	48.6	41.4
% residue of vac dist	17.6	8.3	13.2	11.1	12.6
% total liq product boiling ≤ 218 °C	32.4	26.4	31.5	24.3	26.3
% total liq product boiling ≤ 218 °C and aromatic	28.5	21.7	28.7	22.4	23.9
gas volume (cm^3)	192	139	133	94	120
gas composition:					
% CO	13.6	n.m.[h]	n.m.	n.m.	n.m.
% CO_2	6.1	n.m.	n.m.	n.m.	n.m.
% C_1	4.4(5.5)[i]	1.7	0.7	0.3	0.8
% C_2 ethylene	1.3(1.6)	2.0	1.0	0.9	1.6
% C_2 ethane	6.0(7.5)	4.5	1.7	1.5	1.5
% C_3	56.7(70.6)	72.6	52.3	49.5	52.4
% C_4	11.1(13.8)	19.3	33.2	35.0	34.1
% C_5	0.8(1.0)	----	11.1	12.7	10.0

Table 6. Continued ...

[a] Diameter of micro-reactor: 0.635 cm

[b] Catalyst: HZSM-5 (1 g)

[c] In order to collect sufficient product for analysis the products from duplicate runs were combined.

[d] See Table 2.

[e] See Table 2. Note that the heating period in the modification step was 4 h.

[f] See Table 2. Note that a $CO-H_2$ mixture was used in the modification step.

[g] Calculated assuming an average molecular weight of 40.

[h] Not measured, due to instrumental difficulties.

[i] Calculated excluding CO and CO_2, to enable comparison with results in runs where the CO and CO_2 were not measured.

Table 7. Upgrading experiments: upgrading of batch reactor oils, effect of temperature[a,b]

Run Number[c]	U61/62	U63/64	U65/66	U67/68	U69/70	U71/72
Variables:						
Feed Oil	B-367[d]	B-367	B-367	B-367	B-367	B-367
Temp (°C)	370	390	350	390	390	390
Duration (h)	1	1	1	1	1	0.5
VHSV	2	2	2	2	2	4
wht % liq produced	62.7	64.6	54.9	63.6	64.4	65.9
wht % gas produced[e]	6.3	8.0	6.1	7.7	7.8	6.8
wht % coke produced	31.0	27.4	39.0	28.7	27.8	27.3
Analysis:						
relative to feed oil						
% liq product vac dist	54.2	51.1	43.8	47.4	47.6	50.3
% residue of vac dist	8.5	13.5	11.1	16.2	16.8	15.6
% total liq product boiling ≤ 218°C	34.7	35.6	26.9	30.8	30.5	31.2
% total liq product boiling ≤ 218°C and aromatic	31.3	32.5	23.7	28.3	27.4	28.2
gas volume (cm^3)	135	162	126	171	157	152
gas composition:						
% CO	n.m.[f]	n.m.	n.m.	n.m.	n.m.	n.m.
% CO_2	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
% C_1	1.5	2.0	0.5	1.9	1.9	1.0
% C_2 ethylene	4.2	1.7	1.4	1.5	2.7	1.6
% C_2 ethane	2.9	3.8	2.2	3.8	3.8	2.7
% C_3	63.5	71.0	67.2	71.8	70.3	69.6
% C_4	24.5	19.4	25.2	19.0	19.3	22.7
% C_5	3.0	2.0	3.1	1.8	2.1	2.3

Table 7. Continued ...

[a] Diameter of micro-reactor: 0.635 cm.

[b] Catalyst: HZSM-5 (1 g)

[c] In order to collect sufficient product for analysis the products from duplicate runs were combined.

[d] See section 4.3.2.1.

[e] Calculated assuming an average molecular weight of 40.

[f] Not measured, due to instrumental difficulties.

Table 8. Upgrading experiments: upgrading of batch reactor oils, effect of addition of water[a,b]

Run Number[c]	U73/74	U75/76	U77/78	U79/80
Variables:				
Feed Oil	B-379[d]	B-379	B-379	B-379
Water:Oil	0	3:1	1:1	0.55:1
Temp (°C)	370	370	370	370
Duration (h)	0.5	0.5	0.5	0.5
VHSV	4	4	4	4
wht % liq produced	57.5	79.4	78.6	77.7
wht % gas produced[e]	5.9	8.2	7.4	6.4
wht % coke produced	36.7	12.4	14.0	15.9
Analysis:				
relative to feed oil				
% liq product vac dist	44.8	51.9	52.9	54.1
% residue of vac dist	12.7	27.5	25.7	23.6
% total liq product boiling ≤ 218°C	29.6	35.4	33.6	37.4
% total liq product boiling ≤ 218°C and aromatic	25.9	29.8	29.1	33.0
gas volume (cm^3)	134	170	159	145
gas composition:				
% CO	n.m.[f]	n.m.	n.m.	n.m.
% CO_2	n.m.	n.m.	n.m.	n.m.
% C_1	1.2	0.4	0.3	0.3
% C_2 ethylene	4.0	16.5	11.7	6.9
% C_2 ethane	2.1		0.8	0.9
% C_3 propene	7.0	49.0	21.6	15.8
% C_3 propane	55.1		29.9	35.6
% C_4 isobutane, isobutene 1-butene, isobutylene	16.3	32.9	21.0	21.9
% C_4 n-butane	11.0		10.2	13.2
% C_5 pentene	3.1	1.2	2.7	3.4
% C_5 pentane			1.6	1.8

Table 8. Continued ...

[a] Diameter of micro-reactor: 0.635 cm

[b] Catalyst: HZSM-5

[c] In order to collect sufficient product for analysis the products from duplicate runs were combined.

[d] See section 4.3.2.1.

[e] Calculated assuming an average molecular weight of 40.

[f] Not measured, due to instrumental difficulties.

Table 9. Upgrading experiments: upgrading of batch reactor oils, use of various catalysts.

Run Number	U81/82[a]	U84[b]	U85[b]	U86[b]	U87[b]
Variables:					
Feed oil	B-383[c]	B-387[c]	B-387[c]	B-387[c]	B-387[c]
Temp (°C)	370	370	370	370	370
Duration (h)	0.5	0.66	0.66	0.66	0.66
VHSV	4	2.5	2.5	2.5	2.5
Catalyst (5.0 g)	0.5% Pd on 4-8 mesh granualar carbon	0.5% Pd on 0.318 cm alumina pellets	0.5% Pt on 0.318 cm alumina pellets	HZSM-5	0.5% Rh on 0.318 cm alumina pellets
wht % liq produced	52.4	57.6	59.7	55.7	56.1
wht % gas produced[d]	6.7	7.7	8.1	6.3	7.1
wht % coke produced	40.9	34.8	32.2	38.0	36.8
Analysis:					
relative to feed oil					
% liq product vac dist	48.3	48.0	49.7	47.4	47.8
% residue of vac dist	4.1	9.6	10.0	8.3	8.3
% total liq product boiling ≤ 218°C	32.5	34.5	32.6	32.2	31.4
% total liq product boiling ≤ 218°C and aromatic	17.4	17.6	17.5	28.8	17.0

..../2

Table 9. Continued ...

Run Number	U81/82[a]	U84[b]	U85[b]	U86[b]	U87[b]
gas volume (cm^3)	146	245	320	255	265
gas composition:					
% CO	n.m.[e]	16.8	10.6	5.9	19.0
% CO_2	n.m.	22.4	32.2	2.4	22.4
% C_1	17.2	10.7(17.6)[f]	12.7(22.2)	1.1(1.2)	24.6(42.0)
% C_2 ethylene	19.4	2.4(3.9)	0.9(1.6)	0.6(0.7)	1.0(1.7)
% C_2 ethane		8.6(14.1)	11.4(19.9)	2.6(2.8)	4.7(8.0)
% C_3 propene	25.6	9.0(14.8)	6.3(11.0)	68.8(75.0)	6.8(11.6)
% C_3 propane		13.2(21.7)	9.4(16.4)		8.6(14.7)
% C_4 isobutane, 1-butene, isobutene, isobutylene	19.9	6.0(10.0)	4.3(7.5)	11.0(12.0)	4.9(8.4)
% C_4 n-butane		5.5(9.0)	5.7(10.0)	6.3(6.9)	4.2(7.2)
% C_5 pentene	17.9	1.5(2.5)	1.2(2.1)	0.9(1.0)	1.2(2.0)
% C_5 pentane		2.7(4.4)	3.0(5.2)	0.3(0.3)	2.3(3.9)
% C_6	-	1.3(2.1)	2.3(4.0)	0.1(0.1)	0.3(0.5)

a Diameter of micro-reactor; 0.635 cm. Duplicate runs.

b Diameter of reactor: 1.27 cm.

c See section 4.3.2.1.

d Calculated assuming an average molecular weight of 40.

e Not measured, due to instrumental difficulties.

f Calculated excluding CO and CO_2, to enable comparison with results in runs where the CO and CO_2 were not measured.

Table 10. Upgrading experiments: upgrading of batch reactor oils, use of various catalysts.

Run Number[a]	U88	U89	U90	U91	U92
Variables:					
Feed oil	B-391[b]	B-391[b]	B-391[b]	B-391[b]	B-391[b]
Water:oil	0	0	0	1:1	1:1
Temp (°C)	370	370	370	370	370
Duration (h)	0.66	0.66	0.66	0.66	0.66
VHSV	2.5	2.5	2.5	2.5	2.5
Catalyst (5.0 g)	0.5% Ru on 0.318 cm alumina pellets	0.5% Pd on 4-8 mesh granular carbon	3 mm glass beads	HZSM-5	0.5% Ru on 0.318 cm alumina pellets
wht % liq produced	63.8	45.7	80.9	75.5	71.4
wht % gas produced	6.6	8.2	1.2	5.8	4.7
wht % coke produced	29.6	46.1	17.9[c]	18.7	23.9
Analysis: relative to feed oil					
% liq product vac dist	51.6	43.5	57.0	53.3	55.9
% residue of vac dist	12.2	2.2	23.9	22.2	15.5
% total liq product boiling $\leq$ 218 °C	33.9	28.2	34.9	33.6	35.4
% total liq product boiling $\leq$ 218 °C and aromatic	17.5	15.9	19.6	29.2	19.6
gas volume (cm^3)	305	398	40	290	232
gas composition:					
% CO	10.1	26.8	n.d.[d]	7.5	2.9
% CO_2	44.5	16.2	n.d.	3.0	69.7
% C_1	18.6 (41.0)[e]	10.8 (18.9)	19.4	0.8 (0.9)	5.0 (18.2)
% C_2 ethylene	1.4 (3.1)	0.6 (1.1)	2.7	7.5 (8.4)	1.7 (6.2)
% C_2 ethane	5.9 (13.0)	12.6 (22.1)	23.5	1.7 (1.9)	1.6 (5.8)
% C_3 propene	6.4 (14.1)	2.2 (3.6)	13.3	6.7 (7.5)	4.0 (14.6)
% C_3 propane	3.0 (6.6)	11.1 (19.5)	17.1	47.7 (53.3)	5.1 (18.6)
% C_4 isobutane	5.0 (11.0)	2.0 (3.5)	2.8	16.7 (18.7)	3.7 (13.5)
1-butene, isobutene isobutylene	1.1 (2.4)	6.3 (11.1)	5.5	6.0 (6.7)	2.9 (10.6)
% C_4 n-butane	1.9 (4.2)	5.2 (9.1)	8.3	1.8 (2.0)	2.7 (9.9)
% C_5 pentene	1.3 (2.9)	2.4 (4.2)	7.5	0.5 (0.6)	0.4 (1.5)
% C_5 pentane	0.8 (1.8)	3.8 (6.7)		0.1 (0.1)	0.3 (1.1)
% C_6					

Table 10 ... Continued ...

[a] Diameter of reactor; 1.27 cm.

[b] See section 4.3.2.1

[c] Softens upon heating and also soluble in acetone.

[d] Not detectable.

[e] Calculated excluding CO and CO_2, to enable comparison with results in runs where the CO and CO_2 were not measured.

Table 12. Carbon analysis using the Parr Calorimeter

SAMPLE	CARBON ANALYSIS (%)	
	CALORIMETER	C-H ANALYSER
A. REFERENCE COMPOUNDS		
Benzoic acid[a]	68.3 , 68.9	
1,2,4-Trimethylbenzene[b]	89.1	
B. ASPEN POPLAR WOOD	47.1 , 46.5	
C. ASPEN POPLAR OIL		
C-58 (Table 1)	66.2[c]	68.7
B-378 (Table 2)	80.1[c]	82.3
B-379	79.8[c], 83.4[d]	81.4
B-381 (Table 2)	78.4[c], 78.9[d]	80.7
B-382	79.8[c], 79.2[c]	80.3

[a] Calculated for C: 68.9%

[b] Calculated for C: 89.9%

[c] Oil was centrifuged at 2000 rpm and the percent carbon calculated to a moisture-free basis.

[d] Oil was centrifuged at 2000 rpm and dried at room temperature for two weeks.

7.1 CONCLUSIONS

The results obtained in the present work shows that batch reactor oil can be upgraded using various catalysts in a micro-reactor. Both HZSM-5, a shape selective zeolite, and transition metals may be used as catalysts. Oil produced in the continuous reactor can be modified in the batch reactor to produce a product which is sufficiently thermally stable to be used as feed for the micro-reactor. Either batch reactor oil or modified continuous reactor oil when treated in the micro-reactor produce essentially the same products with similar yields. The results also show that using water as a co-feed results in a significantly higher liquid product yield and in less coke production. It is also concluded that the use of HZSM-5 produces significantly larger yields of aromatic hydrocarbons than do the transition metal catalysts used. The upgrading studies were limited in that only a small number of catalysts were tried. Also the oil was not fractionated, e.g., by vacuum distillation, with different catalysts being tried on the various fractions.

Studies using the batch reactor show that wood shavings may be used instead of wood meal for producing oil. This fact has economic significance since the cost of producing wood shavings is considerably less than that for wood meal.

The identity of the compound(s) responsible for the modification of continuous reactor oil was not established. It has been concluded however that reducing acid conditions play a role in the modification step.

The cost of constructing and assembling a 7.6 cm inside diameter continuous reactor, plus auxiliary equipment has been estimated to be $258,425.

8.1 RECOMMENDATIONS

Over the past several years, during the period of time that research under this contract has been conducted, a significant decrease in the urgency to find sources of liquid fuels as alternatives to fossil oil has occurred. However, it is not unreasonable to assume that an equally rapid change could take place, whereby once again the need for such substitutes becomes critical. The experience gained and the results obtained during the span of this research should be recognized as a good foundation on which to continue research and, when opportune, to lead to commercial production. For this reason it is strongly recommended that, if at all possible, research in this area be continued. The following specific recommendations are thought to be suitable and important areas for further study.

1. Although the small-scale continuous reactor has been thoroughly tested and shown to be very satisfactory as a means of converting dry wood meal into an oil fraction it was limited by the restriction on temperature (360 ^{o}C) at which the reaction could occur. Studies on modification of the continuous oil in a batch reactor at 390^{o}C, showed that at the higher temperature an improved oil product is obtained and which, in turn, is more suitable for upgrading in a micro-reactor over a HZSM-5 (zeolite) catalyst to produce aromatic hydrocarbons. It may well be that a modification of the continuous reactor so that it would be operated at 390^{o}C, would permit of a one-stage continuous preparation of the higher quality oil.
2. Studies on the mechanism whereby continuous reactor oil may be modified by further heating it, along with the aqueous phase produced at the same time, in a batch reactor at 390^{o}C, have revealed that there are components in the aqueous phase that are responsible for the modification. Attempts

to isolate and identify any such pure substances were initiated but were only partly successful. A fuller understanding of the nature of the reactions involved is important. Should it be found that certain compounds are responsible for the oil modification, new and simpler routes to oil improvement could be devised.

3. More batch runs using wood shavings should be made. The one run (B-384) made in the present work resulted in the production of a very fluid oil containing only 7.3% oxygen. This result should be verified. This value for the oxygen content is comparable with that produced in the batch modification of continuous reactor oil. The thermal behaviour of the oil should also be tested to find out if it could be used as feed for the micro-reactor. If wood shavings are to be considered as feed for a larger scale continuous reactor then such studies are important.
4. A reactor of approximately 7.6 cm inside diameter should be constructed if further work on the use of a continuous reactor using dry feed stock is to be done. A reactor of about this size would appear to be the next logical step before a pilot plant is considered.
5. Upgrading studies should be continued. The following points should be considered:
   a) The use of a larger number of different catalysts.
   b) A larger variation of the operating variables, e.g., temperature and VHSV (volume hourly space velocity).
   c) More extensive study of the use of water as a co-feed with the oil.
   d) Fractionation of the feed oil, e.g., by vacuum distillation, followed by an investigation of the upgrading of each fraction.

   It appears reasonable to expect that improved yields of desirable products and a decreased yield of coke would be the result of an extensive study following points a) to d) above.

9.1 REFERENCES

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